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Determination of Crystalline Silica in Dust at Low Concentrations by Low-Temperature Infrared Spectrometry

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Abstract

The American Conference of Governmental Industrial Hygienists (ACGIH) accepted a lower threshold limit value (TLV) for respirable crystalline silica (RCS) exposure of 25 $\mu g/m^3$, half of the previous TLV. This change is problematic because the current standard sampling and measurement practices used by NIOSH, OSHA, and MSHA are not sensitive enough to allow an analyst to confidently determine samples acquired near the TLV. In response to this need for a more sensitive method to analyze respirable dust filter samples for crystalline silica, a modification of current NIOSH infrared spectrometric methods is being developed. The additional sensitivity is gained by performing the infrared absorbance measurements at 77 K where absorbance peaks are more intense by virtue of being narrower. A quick-change cryostat has been fabricated such that a sample can be introduced to the spectrometer and cooled to 77 K in 5 min, interrogated for 1 min, and removed and the cryostat readied for another sample in 2 min, for a turnaround time of 8 min per sample, which is brief compared to the time required to prepare and redeposit a sample. Therefore, samples can be acquired and interrogated with legacy samplers, filters, pumps, spectrometers, and sample preparation, the only modification being the addition of a cryostat to the spectrometer. Preliminary experiments demonstrate that the peak-to-background ratio of the quartz signature band near 800 cm^{-1} increases by approximately 50 % on cooling from room temperature to 77 K. The slopes of the calibration curve derived from standards interrogated at both room temperature and 77 K indicate that the low-temperature method is approximately 25 % more sensitive.

Keywords

respirable quartz dust; silica dust; FTIR

Introduction

The health hazards of silicosis and black lung disease because of occupational exposure to respirable crystalline silica (RCS) have been known for centuries and have been the subject of much study and regulation in the United States and elsewhere [1]. These very debilitating diseases usually appear after some years of exposure and a period of latency that

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complicates attempts to correlate exposure to disease risk. Crystalline silica remains a topic of interest because of the large number of workers exposed to it, as many as 1.7×10^6 in the United States [1]. The regulations instituted by the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), and the Mine Safety and Health Administration (MSHA) decades ago have made a significant impact on the number of deaths in the United States because of RCS. For example, deaths from silicosis were lowered by a factor of approximately six between 1968 and 2004 [1]. Nevertheless, RCS is still a significant occupational health hazard, with approximately 500 deaths from black lung disease and 150 deaths from silicosis in 2004 [1]. In addition to silicosis and black lung disease, there are other disease hazards associated with exposure to RCS. The American Conference of Governmental Industrial Hygienists (ACGIH) decided, based on the increased risk of cancer in workers with pulmonary fibrosis from silica exposure, that the threshold limit value-time weighted average (TLV-TWA) of RCS be set below the current NIOSH recommended exposure limit of 50 $\mu g/m^3$ to 25 $\mu g/m^3$ [2]. In addition to the identification of lung cancer hazard [3], other health hazards from chronic exposure to RCS recently identified include higher risks of tuberculosis and auto-immune disease [4–6]. For these reasons, even though the RCS hazard has been under scrutiny and regulation for decades, further reductions in exposure are being proposed to protect workers.

In any attempt to regulate occupational exposure to RCS, it is implicit that practical methods to measure exposures at or below the regulatory level are available. For the current TLV value of RCS (usually in the form of quartz) exposure of 50 $\mu g/m^3$, standard methods include NIOSH 7500, NIOSH 7602, NIOSH 7603, OSHA ID-142, and MSHA P-7. They are all based on acquiring samples on filters by pumps drawing air at 1.7 to 2.21/min. For example, at the current REL (recommended exposure limit, 50 $\mu g/m^3$) of quartz, an 8-h sample drawn at 1.71/min will deposit 40.8 μg of quartz on a filter. These methods state a limit of detection of 5 μg or higher, which means that the limit of quantitation (LOQ), defined as 3.3 times the LOD (limit of detection) is 17 μg [7]. This level of sensitivity is adequate to monitor the older TLV; i.e., 40.8 μg of quartz on a filter is quantifiable. This LOQ is marginally adequate for the newest ACGIH TLV when a sample is drawn for less than 8 h, which frequently happens. Ultimately an analyst must be able to state with reasonable confidence that a measured value of quartz below the TLV indicates that the worker involved in the measurement was truly not exposed to excessive respirable quartz. In the case of a 4-h sample (i.e., a half-shift) at 1.71/min at the 25 $\mu g/m^3$ concentration of respirable quartz dust, the analyst must quantify 10 μg of quartz. If the analyst cannot state with certainty whether or not the quartz mass exceeds this amount, then either the new ACGIH recommendation cannot be implemented or a sampling system of higher flow rate must be deployed wherever there is exposure to respirable quartz dust. Although current methods can meet this criterion, they do so barely, leaving the analyst very little margin for error [8–10]. The best resolution would be to develop a method of quartz measurement that is reliable well below 10 μg.

There are currently three approaches to determining quartz in dust samples included in the NIOSH *Manual of Analytical Methods*. The oldest is a wet chemical method, NMAM 7601

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[11]. It uses the visible absorption of a silicomolybdate complex to determine the amount of silicon in an ashed sample after all forms of silicon-containing material except quartz have been removed by phosphoric acid. The limit of detection of this method is 10 μg. There are some problems [12] affecting the accuracy of this method when certain other silicates besides crystalline silica are present in the sample. It has also been reported that the precision of the method is particularly sensitive to the skill of the analyst in executing the procedure [12]. This method is labor-intensive and is no longer widely used. It is unlikely that any attempt to lower the LOD of this method by minor changes would be fruitful; there are inherent limitations that cannot be readily overcome.

The second approach to determination of quartz in dust uses the intensity of diffracted X rays at the angle characteristic of α-quartz. This is the approach of NMAM 7500 [11], MSHA P2 [13], OSHA ID-142 [14], and the United Kingdom's Health and Safety Laboratory Methods for the Determination of Hazardous Substances (MDHS) 101 [15]. NMAM 7500, MSHA P2, and OSHA ID-142 require that dust samples be removed from the filters on which they were collected and re-deposited on a silver membrane for the X-ray analysis, and are very similar except in the techniques used to remove the dust from the filter so that it can be re-deposited for analysis. The methods report total crystalline silica, but in fact the X-ray measurement distinguishes all the crystalline polymorphs of silica. The X-ray methods have at best a 5 μg limit of detection for quartz [12–16]. MDHS 101 omits the re-deposition, but estimates an LOD of 10 μg because of non-linearity. All the X-ray methods specify a lower limit to their useful range of 20 μg. The X-ray diffraction peaks are very specific for every crystalline material, so it is relatively easy to correct for interferences. In many ways, this method is nearly ideal. However, it does have drawbacks, especially the capital cost of the X-ray diffractometer. Also, the method is not equally sensitive to all respirable size particles; the smaller end of the respirable range is measured with less sensitivity than the larger diameter particles [16]. The method has become popular in laboratories that can afford the initial capital expense of an X-ray diffractometer. In looking forward as to how the method could be made more sensitive there are limited avenues to pursue. Current generation X-ray detectors are very efficient, and therefore the only way to improve the X-ray method would be to either generate more X rays or to somehow affect the scattering efficiency of α-quartz. No simple approach to improving either of these methods was readily apparent.

The third technique for quantifying respirable α-quartz is based on the infrared method of crystalline silica determination found in NMAM 7602 and 7603 [11] and MSHA P-7 [17]. (NMAM 7602 uses a potassium bromide pellet to hold the dust sample in the infrared beam. The other methods redeposit the dust on a filter.) They use the characteristic quartz absorption band near 800 cm^{-1} to determine the amount of quartz present in the sample. The methods differ in some details of sample preparation and data analysis but the infrared spectrophotometric aspects are essentially the same. The measured intensity of a peak (either area or peak height) is related to the mass of absorbing molecules by Beer's Law,

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$$\frac{I}{I_0} = e^{-(\in K)}$$

Here, I_0 is the intensity of infrared light incident on a sample, I is the intensity transmitted by the sample, and K is the mass per unit area of the absorbing molecule on the filter that is illuminated by the infrared light. $\in$ is the peak height at one point of the absorption spectrum (or peak area if integrated area is being used) in units of filter area per mass of quartz (i.e., the product $\in K$ must be dimensionless). The logarithm of this ratio is the measured absorbance, and it is the absorbance that is proportional to the mass of quartz on the filter. The various infrared methods report different LODs and different lower limits of ranges of applicability. The LODs are 5 μg quartz for NMAM 7602 and 10 μg quartz for 7603. The reported lower limits of their working ranges are 10 and 30 μg quartz for 7602 and 7603, respectively. One inherent advantage to the infrared method is the low cost. The only expensive capital equipment necessary for these methods is the FTIR instrument itself, and suitable systems have become relatively inexpensive in recent years. The methods are precise, accurate, and relatively quick. Kaolin is an interference commonly found in dusts analyzed for quartz, but the methods include corrections for it. Ainsworth [18] reviewed the history of the methods and discussed some details of sample preparation. She reported an LOD of 4 μg quartz based upon the standard deviation of the filter background in MSHA P-7. Greater sensitivity would be preferable for monitoring concentrations below the current ACGIH TLV, or where it is desired to sample at the TLV for periods shorter than full shift. Diffuse reflection spectroscopy has been demonstrated to quantify quartz mass on a filter as well. Babu in 1993 and 1996 [19,20] presented a linear calibration from 25 μg to 325 μg using a signature peak at 1870 cm^{-1}. The absorption band is far from the interference because of other minerals found in coal mine dust. However, as so far developed, this approach may not enable quantification of quartz masses low enough to monitor compliance with the ACGIH TLV from less than a full shift sample acquisition.

There are in general only three possible approaches to increase the sensitivity of the FTIR absorbance methods of determining quartz mass. They are to increase the intensity of the infrared source, improve the sensitivity of the infrared detector, or increase the value of $\in$ at the frequency at which quartz is measured. As for the first approach, laser sources of continuous, tunable infrared radiation that cover the quartz frequencies are under development but are not available yet. The basic physics of the Nernst glowers that are used in current FTIR spectrometers are unchangeable; there is no way to get significantly more infrared light from them. As for the second approach, the infrared detectors in current FTIR spectrometers are already very efficient. Given the limitations of the methods discussed above, the only avenue to improve the sensitivity of the infrared measurement is the third approach, to modify the spectral characteristics of quartz itself.

The infrared spectrum of any molecule cannot be modified in most respects; it is a unique signature of the molecule in a particular geometric arrangement. There is one feature of the vibrational absorption spectrum of a molecule that can sometimes be modified, and that is the spectral width of a given peak. In the classical, damped harmonic oscillator model of a

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molecular vibration, there are two parameters that describe the resonant response to an applied oscillating field, the natural resonant frequency and the damping constant. The natural resonant frequency is determined by the force constant of the vibration in question. The damping constant is a phenomenological parameter that defines the peak width of the observed transition. At the damped harmonic oscillator level of approximation a resonant line shape is Lorentzian and the total area under a Lorentzian resonant peak is independent of linewidth, i.e., independent of the damping constant [21,22]. Therefore, if a peak can be made narrower, the constant area constraint requires the peak height to increase. Hence, the signal-to-noise ratio at the peak maximum will increase. The Lorentzian peak width (i.e., the inverse of the damping constant) of a given vibrational absorption peak is determined by two mechanisms, population relaxation and pure dephasing [22]. Both of these mechanisms contribute to shortening the lifetime of a vibration excited by an infrared beam, and by Heisenberg's uncertainty principle, the shorter the lifetime the greater the uncertainty, or in this example, the wider the peak width. These mechanisms can be temperature dependent because they originate in the temperature-dependent movement of vibrational energy (phonons) through the crystal lattice; the higher the temperature, the more phonons there are that can perturb the absorbing molecules. (The actual details of the relaxation process that define spectral peak broadening are much more complicated than described here, but a thorough description is far beyond the scope of this work [21–24].) Therefore, it seemed possible that the infrared methods for determining quartz could be made more sensitive by performing the method at low temperatures.

Experimental Approach, Results, and Discussion

To make low temperature spectrometry for determination of quartz practical, it is necessary that an inexpensive quick-change cryostat be used. A suitable arrangement (Fig. 1(a) and 1(b)) comprises a glass cold finger with a Kovar end cap and a copper block soldered to the end cap, the Dew-Johnson cryostat [25]. The copper block is drilled to accommodate a 25 mm filter on one side and a 25 mm magnetic “doughnut” on the other, with a hole in the middle over which the sample deposit is centered and through which the infrared light beam of the spectrometer will pass. A removable steel ring is used to hold the filter in place. The lower section of the cryostat is one piece of glass in the shape of an inverted “T.” The glassware was custom made by Ace Glass Corporation and the copper blocks were fabricated by the NIOSH Morgantown machine shop. The horizontal section holds infrared transparent windows held against O-ring seals. The upright section has an O-ring seal that mates to a seal on the cold finger. There is a vacuum port attached to the lower section by O-ring compression fittings. In operation, a filter is seated in place in the copper block of the cold finger, clamped by the steel ring and magnet. The cold finger is then seated in the Dewar and the Dewar evacuated. A dual stage roughing pump is adequate, but a small turbo pump provides a better vacuum. Both were used in these experiments. In approximately 1 min, the Dewar is evacuated to a medium vacuum. The pressure difference compresses the window and cold finger O-ring seals adequately to seal against leaks. After vacuum is attained the cold finger is filled with liquid nitrogen, approximately 300 ml, not counting boiloff, and the cold finger begins to cool. Any residual water vapor and carbon dioxide will freeze to the cold finger leaving only traces of nitrogen and oxygen in the infrared light path.

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By monitoring changes in the absorption spectrum of a sample it was found that narrowing was complete in approximately 3 min, implying that the filter has reached the temperature of boiling nitrogen, 77 K. Spectral acquisition is complete in less than 1 min, at which point the Dewar is vented and the cold finger with filter sample removed. The cold finger is then allowed to slowly come to room temperature so that the filter can be easily removed and the cold finger loaded with another filter. By having several cold fingers available, samples can be determined every few minutes. Commercial cryostats for infrared spectrometers are available, but typically they are equipped with massive metal cold fingers that require 20 min or more to attain temperature. That long cool down time severely limits the rate at which samples could be determined.

The literature on infrared absorption line-widths in quartz does not include the temperature dependence of line-widths of dusts at low temperatures, so preliminary experiments using re-deposited coal ash samples were performed to compare line-widths of actual coal ash samples at low temperature (77 K) with those at room temperature (300 K), with encouraging results. Further experiments with standard samples of pure quartz were performed. Typical spectra of a 10 μg deposit of NIST 1878a on a DM450 filter are shown in Fig. 2. The bottom frame shows a spectrum recorded under conditions as described in NMAM 7603 at room temperature. The top frame shows the spectrum from the same deposit mounted in the cryostat and recorded at 77 K. The low-temperature peak is noticeably sharper than the room temperature version. From these spectra, it is apparent that the signature peak for quartz near 800 cm^{-1} is significantly enhanced at 77 K as compared to 300 K. To determine the relative sensitivity of this modification of NMAM 7603, five samples each with mass loadings of 1, 2, and 5 μg of quartz were made by pipetting aliquots of a NIST standard quartz (1878a) in alcohol suspension onto DM450 filters as described in NMAM 7603. (NMAM 7603 does not specify standards at such low-mass loadings, but presumably the nominal mass loadings are approximately correct.) The infrared absorbance spectrum of a filter blank was recorded and subtracted from the absorbance spectra of the filters plus quartz. The peak heights above baseline were measured at the peak maxima near 800 cm^{-1} according to the method described in NMAM 7603. Spectra were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, Waltham, MA) operated through the Omnic software package (version 8.1.11, Thermo Fisher Scientific). Samples were held in the Dew-Johnson cryostat for all low-temperature measurements. In Fig. 3 are shown a pair of calibration curves for a single set of NIST standard quartz 1878 a spiked onto DM450 filters as described in NMAM 7603, one curve from data acquired at 77 K and one from data acquired at 300 K. The key feature to note here is that at these very-low-mass loadings, the slope of the low-temperature calibration curve is larger by approximately a third compared to the room temperature curve. By a two-way analysis of variance, the slopes are statistically different ($p < 0.5$).

Conclusion

These preliminary results indicate that by acquiring infrared spectra at temperatures near the temperature of boiling nitrogen, a significant improvement in the LOD and LOQ of NIOSH infrared methods of determining quartz in respirable dusts can be achieved. In the NIOSH method, which uses peak heights, this arises because the net intensity above background of

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the signature infrared absorbance peak for quartz is enhanced at low temperatures. It is feasible to use standard dust samples acquired under typical conditions using conventional hardware and methods in measurements of quartz at levels not previously obtainable. These measurements can be made using conventional FTIR spectrometers with minimal additional equipment and minimal changes to NMAM 7603. Results to date are suggestive of a usable improvement, but a definitive statement about the magnitude of improvement awaits the development of an orthogonal method of calibration. Efforts to address this need are currently underway.

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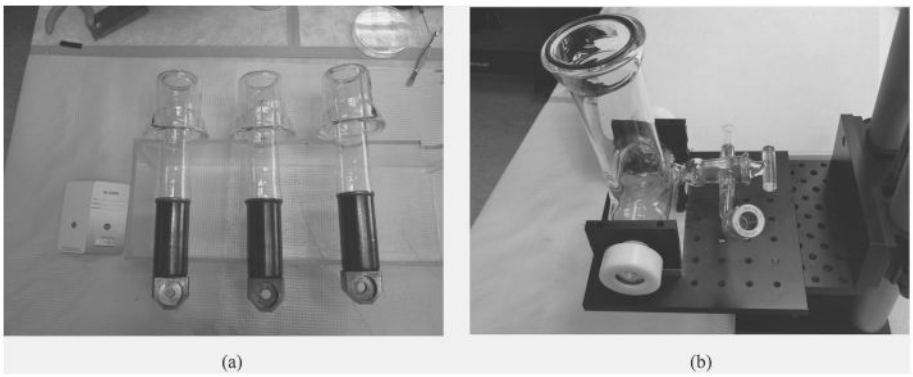

Fig. 1.

(a) A rack of cold fingers for the Dew-Johnson cryostat. A standard IR card is there to indicate the size of the cold fingers. (b) Dew-Johnson cryostat lower inverted-T section. The white caps hold the IR windows in place. The vent and vacuum selection valve is visible on the side, along with the steel O-ring vacuum fitting. The large O-ring joint on top is where the cold finger sits.

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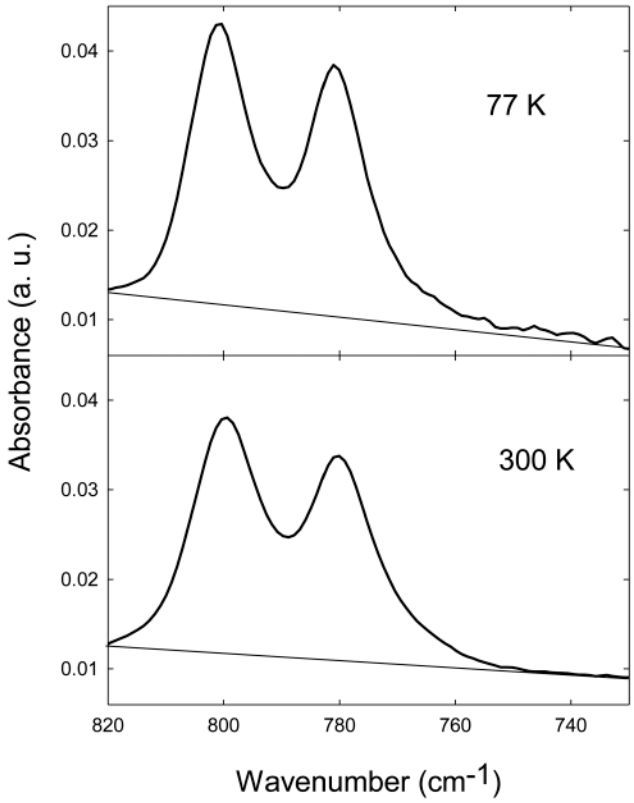

Fig. 2.

Infrared absorption spectra in the region of the 800-cm^{-1} quartz peak of a single sample of 10 μg of 1878a NIST quartz deposited on a DM450 filter. The 300 K spectrum was recorded with the filter mounted in a standard configuration. The 77 K spectrum was recorded with the filter mounted in a Dew-Johnson cryostat equipped with zinc selenide windows.

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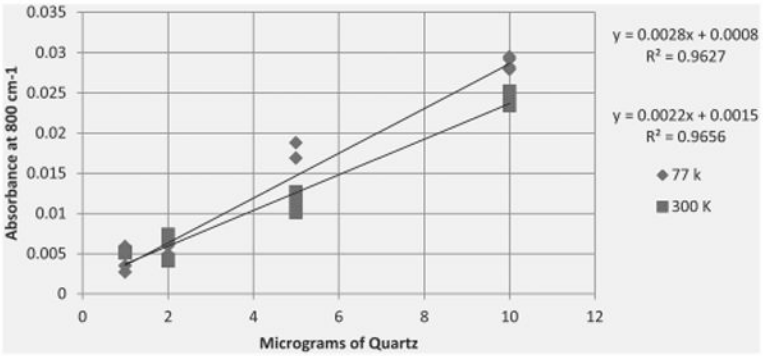

Fig. 3.

Calibration curves from a single set of samples derived from spectra taken measured at room temperature and at 77 K. Peak height above baseline in absorbance units as a function of quartz mass in micrograms. The slope of the calibration at 300 K is .0022; the slope at 77 K is .0028.